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Enclosure 1

SYNTHESIS AND SAXS CHARACTERIZATION OF SULFONATED STYRENE-ETHYLENE/PROPYLENE-STYRENE TRIBLOCK COPOLYMERS

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Introduction

Sulfonated block copolymers have attracted interest in recent years due to their applications in fuel cells,[1] membranes,[2] and elastomers.[3] Sulfonated block copolymers exhibit morphological differences compared to non-ionic counterparts, and the strength of the association of ionic groups increases the Flory-Huggins interaction parameter χ for microphase separation. The increased drive for microphase separation in these systems enables lower block molecular weights while maintaining microphase separation due to the fact that the product χN, where N is the degree of polymerization, is the criterion for phase separation (Fig. 1). Sulfonated styrene-ethylene/propylene-styrene triblock copolymers with short styrene end blocks (~1000 g/mol) and variable length ethylene/propylene (hydrogenated polyisoprene) rubber sequences will be described in this presentation. The importance of the length of the rubber block on morphology and mechanical properties as a function of the critical molecular weight for entanglement is the specific focus of this work.

Small-angle X-ray scattering (SAXS) is critical to the investigation of morphology of traditional ionomers (such as Nafion™), block copolymers, and block copolymer ionomers,[4,5] providing evidence of morphological structure in microphase separated materials. SAXS has been used extensively to characterize the morphology of block copolymers due to Bragg diffraction maxima which identify characteristic microphase separated morphologies in well-ordered samples. SAXS has also been used extensively to study ion-containing polymers. SAXS of ion-containing polymers usually shows a characteristic "ionomer peak" corresponding to a characteristic length scale of 2-6 nm, generally assigned to microphase separated ionic clusters.[4,6,7]

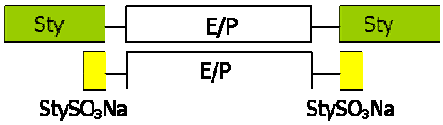

Figure 1. Sulfonated block copolymers (bottom) exhibit phase separation for shorter hard block lengths.

Experimental

Materials. Styrene (99%) and isoprene (99%) monomers were purchased from Aldrich and purified by vacuum distillation from calcium hydride followed by distillation from dibutylmagnesium immediately prior to polymerization. *Sec*-butyllithium (12% in hexanes/heptane) was purchased from FMC Lithium.

Synthesis of Styrene-Isoprene-Styrene (SIS) Triblock Copolymers. Polymerizations were conducted in a 600 mL glass reactor. The reactor was filled with 400 mL dry cyclohexane at 40 °C. 2.06 mL (18.1 mmol) styrene was injected, followed by 1.60 mL *sec*-butyllithium (2.0 mmol, 1.25 M in hexanes) and an orange color rapidly developed. The polymerization proceeded for 5 h and samples were taken at intervals to ensure block formation was complete. Isoprene, 55 mL (550 mmol) was injected and the polymerization was continued for 18.5 h followed by the final styrene aliquot (2.10 mL, 18.1 mmol). SEC analysis revealed block molecular weights of 1.2K-17.1K-0.5K and a molecular weight distribution (M_w/M_n) of 1.01.

Hydrogenation of Styrene-Isoprene-Styrene Triblock Copolymers. Nickel octoate/triethylaluminum hydrogenation catalyst was first prepared by adding triethylaluminum solution (4.8 mL, 4.8 mmol) to nickel 2-ethylhexanoate solution (5.7 mL, 1.34 mmol) in 20 mL cyclohexane. Then, 6.0 g of SIS polymer dissolved in 100 mL cyclohexane was introduced into a glass reactor under N_2. A few drops of catalyst solution were cannulated into the reactor and the reactor was pressurized to 90 psig with hydrogen gas and heated to 50 °C. The hydrogenations were carried out to high conversion, greater than 99%. The catalyst was removed by washing with citric acid solution (10 wt%).

Sulfonation of Styrene-Ethylene/Propylene-Styrene (SEPS) Copolymers. SEPS triblock copolymer (4.20 g) was dissolved in 140 mL cyclohexane and acetyl sulfate (25 equivalents relative to styrene) was generated separately through the addition of sulfuric acid (10.1 g, 101 mmol) to acetic anhydride (16.6 g, 163 mmol) in 1,2-dichloroethane (100 mL) at 0 °C. The acetyl sulfate was added to the polymer solution (at 50 °C). The sulfonation reaction proceeded for 24 h. The polymer was isolated by dripping the crude product into boiling water, removing the solvent by flashing. The polymer was then dialyzed against deionized water. Sulfonated SEPS block copolymer (0.116 g) was dissolved in THF (30 mL) and titrated with standardized 0.023 M NaOH (aq) (0.75 mL) using thymol blue as an indicator. The degree of sulfonation (62%, relative to styrene content) was determined from the average of three titrations. Then, neutralization of a larger portion of polymer (3.89 g) was performed by addition of 45.1 mL (1 equiv) of 0.023 M NaOH.

Small Angle X-Ray Scattering (SAXS) Measurements. Block copolymer samples were cast from THF (SO_3H form) or from toluene/methanol (95/5 w/w, SO_3Na). SAXS data were collected on the Army Research Laboratory SAXS instrument, located at Aberdeen Proving Ground, MD. $Cu_{K\alpha}$ X-ray radiation was generated using a Rigaku Ultrax18 rotating anode X-ray generator operated at 40 kV and 115 mA. A Ni foil was used to filter out all radiation except the $Cu_{K\alpha}$ doublet, with an average wavelength, λ, of 1.542 Å. The ARL instrument uses a Molecular Metrology camera with 300, 200 and 600 μm pinholes for X-ray collimation. Two-dimensional data sets were collected using a Molecular Metrology 2D multi-wire area detector located approximately 1.5 m from the sample. After azimuthal averaging, the raw data were corrected for detector noise, absorption, and background noise. The data were then placed on an absolute scale using a glassy carbon sample 1.07 mm thick, previously calibrated at the Advanced Photon Source of the Argonne National Laboratory as a secondary standard.

SEC, DSC, NMR and DMA Characterization. Size-Exclusion Chromatography (SEC) was performed at 40 °C in HPLC grade tetrahydrofuran at 1 mL/min using a Waters size-exclusion chromatographer equipped with an autosampler, 3 in-line 5 μm PLgel MIXED-C columns. Detectors included a Waters 410 differential refractive index (DRI) detector operating at 880 nm, and a Wyatt Technologies miniDAWN multiangle 690 nm laser light scattering (MALLS) detector, calibrated with PS standards. All reported molecular weight values are absolute molecular weights obtained using the MALLS detector. Differential Scanning Calorimetry (DSC) was performed on a Perkin Elmer Pyris 1 instrument under a nitrogen flush at a heating rate of 10 °C/min. ^{1}H NMR spectroscopic data was collected in $CDCl_3$ on a Varian 400 MHz spectrometer at ambient temperature. Dynamic mechanical measurements were carried out on a TA Instruments Q-800 DMA under nitrogen at a heating rate of 3 °C/min and 1 Hz frequency. The samples were measured in film tension mode, on solvent cast samples.

Results and Discussion

Polymer Synthesis. SIS triblock copolymers were synthesized through sequential monomer addition (Fig. 2). Anionic polymerization techniques allowed control of molecular weight and the synthesis of well-defined block copolymers for subsequent fundamental studies. Narrow molecular weight distributions are critical for establishing known block molecular weights, especially for the synthesis of short (1000 g/mol) endblocks. SEC analysis during the polymerization demonstrated complete conversion of each block in the time intervals chosen, which established the absence of tapering between the blocks. Furthermore, the SEC showed complete crossover between blocks and the absence of dead chains. The final block copolymer molecular weights are tabulated in Table 1. Hydrogenation of the block copolymers was achieved using a conventional nickel/aluminum catalyst which selectively hydrogenated the isoprene blocks. Hydrogenation was important due to the reactivity of olefin groups towards sulfonating reagents. Sulfonation was conducted using acetyl sulfate in a mixture of cyclohexane and dichloroethane (~50:50).

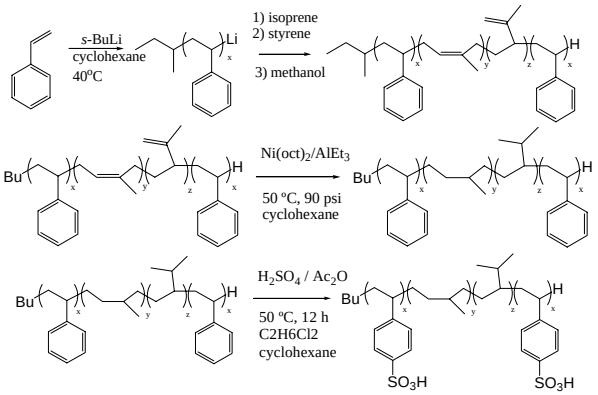

Figure 2. Synthesis of sulfonated SEPS.

Table 1. Compositional Analysis Of Block Copolymers.

Sample	Block Mol. Wt.[a] (g/mol)	M_w/M_n	wt% Styrene[b]	% Sulfonation[c]	T_g (°C)[d]
65A	1.0K-10.0K-0.4K	1.01	12.2	45	-54
114	1.2K-17.1K-0.5K	1.01	9.1	62	-57
65C	1.0K-27.5K-0.8K	1.02	6.1	46	-56

[a] SEC analysis, calculated from block molecular weights adjusted for hydrogenation
[b] ^{1}H NMR analysis
[c] Titration against 0.02 M $NaOH_{(aq)}$ in tetrahydrofuran, as a percentage of styrene monomer
[d] DSC, 10°C/min, N_2

Dynamic Mechanical Analysis. DMA of the sulfonated block copolymers revealed the glass transition of the ethylene/propylene (E/P) rubber phase at approximately -45 °C (Fig. 3). A rubbery plateau exists for the sulfonic acid containing polymers that ranged up to 60 °C, while the rubbery plateau for sodium sulfonate salt reached nearly 150 °C. The high temperature mechanical performance of the ionomers was in agreement with the stronger association of ionic groups (SO_3Na) in comparison to hydrogen bonding groups (SO_3H).

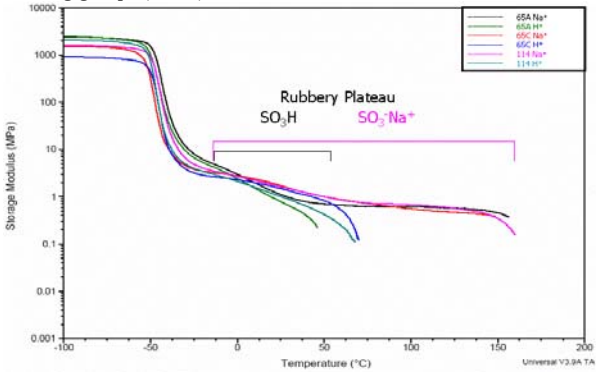

Figure 3. Dynamic mechanical analysis of sulfonated SEPS.

Small Angle X-Ray Scattering Characterization. SAXS is a powerful tool for the analysis of bulk properties of microphase separated systems and is sensitive to electron density fluctuations in ionomers due to the presence of metal counter ions and other heavy atoms such as sulfur. Due to the low degree of polymerization (DP) of the styrene blocks, only the SEPS precursor with the highest styrene volume fraction produced a scattering maximum (q^* = 0.058 $Å^{-1}$). Upon sulfonation, the drive for microphase separation increased, which led to the development of microphase separated morphologies in all cases.

The SAXS experiments in this study indicated the presence of microphase separation in the sulfonated SEPS block copolymers (Fig. 4). The absence of higher-order peaks in the SAXS data revealed a lack of long-range ordering in these materials. The scattering maxima were believed to arise from scattering from the partially sulfonated polystyrene domains which are dispersed in the hydrocarbon ethylene/propylene matrix, akin to the scattering from polyurethane materials.

Comparisons among scattering profiles for polymers with differing rubber block molecular weights indicated that the scattering maxima increased in intensity with decreasing molecular weight. This was expected due to the increase in the sulfonated styrene volume fraction with decreasing rubber content.

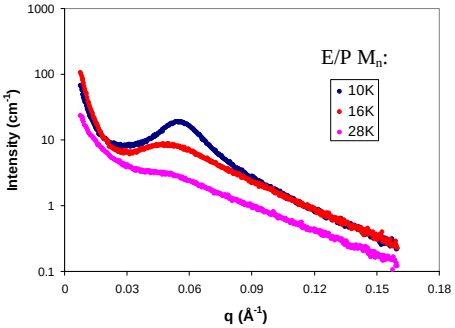

Figure 4. 1-D SAXS profiles for sulfonated SEPS of varying E/P M_n.

The interdomain distances (Bragg spacings) calculated for the sulfonated block copolymers increased with increasing molecular weight (Table 2). A similar trend was observed for the sodium sulfonated form of the block copolymers. Jerome *et al.* observed a similar trend of interdomain spacing with molecular weight for telechelic ionomers, finding that the interdomain spacing was proportional to the root-mean-square end to end distance.[8]

Table 2. Scattering Maxima Positions And Bragg Spacings.

Sample	E/P M_n (g/mol)	Form	q* ($Å^{-1}$)	d (nm)
65A	10	SO_3H	0.055	11.4
65A	10	SO_3Na	0.061	10.3
114	16	SO_3H	0.049	12.6
114	16	SO_3Na	0.053	11.9
65C	28	SO_3H	0.047	13.4
65C	28	SO_3Na	0.049	12.9

The SAXS spectra of the sodium sulfonated polymers featured decreased Bragg spacings compared to the sulfonic acid polymers. The smaller spacing between hard phases may arise from a "tightening" of the physical network structure due to the increased attractive forces between ionic groups when compared to neutral sulfonic acid groups. Furthermore, broader SAXS maxima were observed for the ionomers, indicating hindered morphological development due to ionic association.[7]

Conclusions

Novel, short outer block sulfonated SEPS triblock copolymers were synthesized, characterized via DMA and SAXS. The polymers exhibited microphase separation in which the minor component, sulfonated polystyrene formed a dispersed, hard phase in the soft, ethylene/propylene rubber matrix. The interdomain spacing measured by SAXS allowed an analysis of the effects of the rubber block molecular weight and neutralization.

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